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METHODS FOR THE ANALYSIS OF INSECTICIDES AND FUNGICIDES.

GENERAL DISCUSSION.

Samples of paris green, London purple, soft soap, copper carbonate, and tobacco extracts are to be thoroughly mixed before analysis, taking care that the first two samples are not further pulverized. Samples of lye and potassium cyanide are to be weighed in large quantities in weighing bottles and aliquot portions from a water solution taken for analysis.

PARIS GREEN.

MOISTURE.¹

Dry 1 to 2 grams for eight to ten hours at 105°–110° C. and calculate the loss as moisture. (In duplicate.)

TOTAL ARSENIOS OXID. METHOD I.¹

Solutions required.—A starch solution is used which is prepared by boiling 2 grams of starch with 200 c. c. of water for about five minutes.

A standard iodine solution is prepared in the following manner: Dissolve 12.7 grams of powdered iodine in about 250 c. c. of water to which has been added 18 to 25 grams of c. p. potassium iodide, and make the whole up to a volume of 1 liter. To standardize this solution, weigh out 1 gram of the inclosed dry c. p. arsenious oxide, transfer to a 250 c. c. flask by means of about 100 c. c. of a solution containing 2 grams of sodium hydrate in each 100 c. c. and boil until all arsenious oxide goes in solution, make to a volume of 250 c. c., and use 50 c. c. for analysis.

This 50 c. c. portion is concentrated by boiling in a 250 c. c. flask to half its volume and allowed to cool to 80° C. An equal volume of concentrated hydrochloric acid is now added, accompanied by 3 grams of potassium iodide, mixed, and the whole allowed to stand for ten minutes (to reduce the arsenic oxide, formed on boiling an alkaline arsenite, to arsenious oxide). The brown solution is then diluted with cold water and an approximately N-10 solution of sodium thiosulphate added, drop by drop, until the solution becomes exactly colorless. (This end point is easy to read without the aid of starch.) This solution is then made slightly alkaline with dry sodium carbonate (using a drop of methyl orange to read the change), then made slightly acid with hydrochloric acid, *taking care that all lumps of sodium carbonate on the bottom are acted on by the hydrochloric acid.* Sodium bicarbonate is now added in excess and the solution of iodine run in, drop by drop, using starch solution to read the end reaction. (Sometimes the solution gets dark toward the end of the titration. This must not be confused with the final dark-blue color given by the iodine and starch.)

From the number of cubic centimeters of iodine solution used and the weight

¹ Haywood, Jour. of the Am. Chem. Soc., Vol. XXII, No. 9.

of arsenious oxid taken, the value of each cubic centimeter of iodine in arsenious oxid can be determined.

Method.—Two grams of paris green are weighed out and transferred to a 250 c. c. flask and about 100 c. c. of water and 2 grams of sodium hydrate added. This solution is boiled for five to ten minutes, or until all of the green particles have changed to red cuprous oxid. It is then cooled to room temperature and the volume made to 250 c. c. The well-shaken liquid is filtered through a dry filter and 50 c. c. taken for analysis. The analysis is carried out from this point forward the same as when we standardize the iodine solution. (In duplicate.)

TOTAL ARSENIOS OXID. METHOD II.¹

Solutions required.—The solutions required are the same as those mentioned in Method I with the addition of a solution containing 2 to 3 grams of sodium potassium tartrate dissolved in 50 c. c. of water.

Method.—Sample the paris green (as one would an ore for assaying) down to about 1 gram. Pulverize this small sample in an agate mortar and weigh out 0.2 to 0.3 gram in a beaker of, say, 300 c. c. capacity. Add 25 c. c. of water, and to the green suspended in the water add, with constant stirring, concentrated hydrochloric acid till solution is just effected. Six to 12 drops are usually sufficient. Now add to the acid solution sodium-carbonate solution till a slight permanent precipitate is formed. Dissolve this precipitate by adding 2 to 3 grams of sodium potassium tartrate in solution. Now dilute to about 200 c. c., add solid sodium bicarbonate and starch solution, and titrate with iodine in the usual way. (In duplicate.)

SOLUBLE ARSENIOS OXID. METHOD I.²

Solutions required.—A solution of starch and standard iodine prepared as above and a solution of sodium acetate containing 12.5 grams of the crystallized salt in each 25 c. c.

Method.—Digest over the flame 1 gram of paris green for about five minutes with 25 c. c. of a solution of sodium acetate containing 12.5 grams of the crystallized salt. The solution is then cooled, made up to 100 c. c., and 50 c. c. filtered off and titrated with standard iodine in the usual way. (In duplicate.)

SOLUBLE ARSENIOS OXID. METHOD II.³

Solutions required.—A starch and standard iodine solution prepared as above.

Method.—One gram of paris green is treated with 1,000 c. c. of water (previously boiled to get rid of CO_2 and again cooled to room temperature) in a large flask. The flask is stoppered and shaken 8 or 10 times each day for ten days. At the end of this time the solution is filtered off through a dry filter. Two hundred cubic centimeters of this are treated with sodium bicarbonate and titrated with iodine. This will give the percentage of arsenious oxid dissolved.

Another 200 c. c. of the solution is treated with 5 c. c. of concentrated hydrochloric acid, heated to 70°C. , and a current of H_2S passed through until all arsenic and copper are precipitated. It is then filtered and washed quickly with hot water. The filter and its contents are burned with powdered sulphur and weighed in a porcelain crucible. In this way a mixture of CuO and Cu_2S is obtained. To calculate the percentage of CuO dissolved, consider the residue as entirely made up of CuO . This will be correct, since the per cent of copper in CuO and Cu_2S is the same. (In duplicate.)

¹ Avery-Beans, Jour. of the Am. Chem. Soc., Vol. XXIII, No. 7.

² Avery-Beans, Jour. of the Am. Chem. Soc., Vol. XXIII, No. 2.

³ Haywood, Jour. of the Am. Chem. Soc., Vol. XXII, No. 9 and Vol. XXII, No. 10.

Please send both the figures for arsenious oxid and cuprous oxid dissolved by Method II.

TOTAL COPPER OXID. METHOD I.¹

Solutions required.—A standard approximately N-10 solution of sodium thio-sulphate is prepared by first dissolving 24.8 grams of the crystallized salt in a liter of water. This solution is standardized by the method of analysis given in the following paragraph, using the inclosed c. p. copper with which to make copper nitrate solution of known strength.

Method.—The cuprous oxid obtained in Method I above, for total arsenious oxid by boiling the paris green with sodium hydroxid, is poured on the filter (after taking an aliquot portion of the solution for the determination of arsenious oxid) and well washed with hot water. It is then dissolved with hot dilute nitric acid and made to a volume of 250 c. c., one-fifth being taken for analysis. The copper in solution is determined in the following manner:

The nitric acid solution is made alkaline with sodium carbonate; then made slightly acid with acetic acid, diluted with water and about ten times the weight of the copper in potassium iodid added. When it is all dissolved, the free iodine is titrated with a standard solution of sodium thiosulphate, using starch as indicator. The full details of this method are given in Sutton's "Volumetric Analysis," third edition, page 133. (In duplicate.)

TOTAL COPPER OXID. METHOD II.

Solutions required.—A fifth normal solution of potassium cyanide is prepared, which is standardized against a known weight of copper dissolved in nitric acid, the method being the same as that described in the next paragraph.

Method.—An aliquot portion of the nitric acid solution of copper oxid in Method I, for total copper oxid, is neutralized with sodium carbonate and a trifling excess added. One cubic centimeter of .960 sp. gr. ammonia is added and the dark blue solution titrated with the standard potassium cyanide. The discussion of this method is given under copper in Sutton's "Volumetric Analysis." (In duplicate.)

LONDON PURPLE.

MOISTURE.²

Dry from 1 to 2 grams of the substance for twelve to fourteen hours at a temperature of boiling water. (In duplicate.)

TOTAL ARSENIOS OXID.²

Solutions required.—These are starch solution and standard iodine, both prepared as described under "Paris green."

Method.—Two grams of London purple are dissolved in about 80 c. c. of water and 20 c. c. of hydrochloric acid at a temperature of from 60° to 70°, filtered, and washed to a volume of 300 c. c. One hundred cubic centimeters of this is treated in a 500 c. c. flask with sodium bicarbonate in excess. The contents of the flask are then brought to the mark with water, using a few drops of ether to destroy bubbles, and 250 c. c. filtered off. To this is added starch solution and the standard iodine solution until the blue color appears. The result is the arsenious oxid as such, in 50 c. c. of the original solution, or .3333 grams of the original substance. (In duplicate.)

TOTAL ARSENIC OXID.²

Solutions required.—These are the same as those described above for total arsenious oxid.

¹ Haywood, Jour. Am. Chem. Soc., Vol. XXII, No. 9.

² Haywood, Jour. of the Am. Chem. Soc., Vol. XXII, No. 12.

Method.—Fifty c. c. of the hydrochloric acid solution of London purple prepared above (representing .33333 gram) is heated to 80° on the water-bath, and then taken off and 50 c. c. of hydrochloric acid and three grams of potassium iodid added. The mixture is allowed to stand for at least fifteen minutes, the “ic” arsenic thus being reduced to “ous” arsenic by the action of the potassium iodid in the acid solution, iodine being set free. The solution is then rinsed out in a large beaker and tenth-normal sodium thiosulphate added, drop by drop, to get rid of the iodine. The end-point here is rather difficult to read on account of the very dark color of the solution, but with a little practice the chemist can determine it very easily by proceeding as follows:

The sodium thiosulphate is run in a little at a time and occasionally a drop of the solution is added to a drop of starch paste. This will, of course, give a blue color with the starch, which becomes fainter and fainter as the iodine is used up. Finally, when a drop of the solution only gives the slightest blue color with the starch, a little starch paste is added directly to the whole solution and the blue color dissipated with a few drops of thiosulphate. With a little practice the chemist can in this way get the exact end-point every time. The solution is immediately made alkaline with solid sodium carbonate. It is again made slightly acid with hydrochloric acid, taking care that all of the solid particles of the sodium carbonate on the bottom are neutralized by the acid and finally made alkaline with sodium bicarbonate. Starch paste is now added and tenth-normal iodine until the blue color appears. This end-point is easily read if the beaker is placed on a white surface between the eye and the light and iodine run in until a distinct purple color appears. The figure thus obtained gives the number of cubic centimeters of iodine corresponding to the total amount of arsenic in the solution as arsenious oxide. Subtracting from this the number of cubic centimeters of iodine corresponding to the arsenious oxide in the method above, we have left the number of cubic centimeters of iodine corresponding to the arsenic oxide in .3333 grams of the sample. (In triplicate.)

SOLUBLE ARSENIOUS OXIDE.¹

Solutions required.—These are starch and standard iodine prepared as above.

Method.—Extract 1 gram of London purple with 500 c. c. of cold carbon-dioxid-free water for 10 days, by the same method as described in Method II for soluble arsenious oxide in Paris green. Filter off 100 c. c. of the solution through a dry filter and titrate with standard iodine and starch solution in the ordinary manner. The result is soluble arsenious oxide in .2 gram of the original substance. (In duplicate.)

SOLUBLE ARSENIC OXIDE.¹

Solutions required.—These are the same as those described under soluble arsenious oxide.

Method.—To determine the soluble arsenic oxide, an aliquot portion of the water extract from the determination of soluble arsenious oxide above (say 200 c. c.) is transferred to a flask, made slightly alkaline with NaOH, and evaporated to about 25 c. c. on a hot plate. The flask is then removed and allowed to cool to about 80°, and an equal volume of concentrated hydrochloric acid and 3 grams of potassium iodide added. It is allowed to stand fifteen minutes, the iodine set free, exactly used up with tenth-normal thiosulphate by use of starch, if necessary, and the solution neutralized with sodium carbonate. It is again made slightly acid with hydrochloric acid, taking care that all lumps of sodium carbonate are acted on, then made alkaline with an excess of sodium bicarbonate and titrated with iodine, using starch as an indicator. From this figure is

¹ Haywood, Jour. of the Am. Chem. Soc., Vol. XXII, No. 12.

subtracted the figure representing the amount of soluble arsenious oxid and the remainder is calculated as arsenic oxid. (In triplicate.)

COPPER CARBONATE.

COPPER OXID.

Solutions required.—These are the same as those described under the determination of total copper oxid in paris green.

Methods.—A weighed quantity of the substance is dissolved in nitric acid and the same methods of analysis employed as are given under the determination of total copper oxid in paris green. (In duplicate.)

POTASSIUM CYANIDE.

CYANOGEN.

Solutions required.—A tenth-normal solution of silver nitrate.

Method.—A large quantity of the sample is weighed out in a weighing bottle, dissolved in water and made up to a definite volume. Aliquot portions of this are taken for analysis. The N-10 silver nitrate solution is added a drop at a time until one drop produces a permanent turbidity. One eq. of silver is equal to 2 eq. of cyanogen. The cyanogen obtained is calculated to potassium cyanide. Full details of this method will be found in Sutton's "Volumetric Analysis," under cyanogen.

SOAP.

GENERAL STATEMENT.

In compliance with the recommendation of the referee of last year, the present referee has cut out many of the methods of analysis for soap and has only chosen those which show the value of the soap from the entomologist's point of view, i. e., the moisture, so as to give the entomologist some idea of how much true soap is present; and the alkalies, to tell whether a potash or soda soap is in question.

MOISTURE.

The following method is given by Benedikt and Lewkowitsch for determining water in soap. Tare accurately a beaker of 100 c. c. capacity, the bottom of which is covered with recently ignited perfectly dry sand about one-half inch deep, together with a small glass rod.

Weigh off in the beaker about 5 grams of the sample; add 25 c. c. of alcohol; dissolve the soap in the water bath with stirring; evaporate the alcohol, and finally dry in an oven at 110° C. until the weight is constant. A few precautions may be taken, which are not mentioned in the above method, viz: If the soap is hard, the 5 grams should be cut off in thin strips, so as it will dissolve more readily in the alcohol; also, all samples of soap worked upon by the referee never come to a constant weight on drying, but finally commence either to gain or lose a little indefinitely. It is, therefore, best to heat the soap at 110° C. until it is nearly dry and weigh. Return the soap to the oven and dry another half hour. Continue this alternate drying and weighing until the weight only changes a few milligrams during the course of half an hour's drying.

TOTAL ALKALI.

A weighed quantity of the soap is decomposed by hydrochloric acid and the water is filtered off from the fat, which is washed. Both potassium and sodium in the filtrate are first determined as the mixed chlorids in the ordinary manner and the potassium then determined by means of platinum chlorid.

A rapid but only approximate determination of the total alkali in soap is made in the following manner: Weigh out a small quantity of the soap; treat with concentrated sulphuric acid; burn; repeat treatment with sulphuric acid and burn again. Add a small amount of ammonium carbonate to the dish, cover

and heat. Repeat this a number of times till all bisulphates have changed to sulphates. Test the residue in the flame to see whether it is sodium or potassium sulphate and calculate the residue to soda or potash, as the case may be.

SODA LYE.

CARBONATE AND HYDROXID. METHOD I.

Solutions required.—A normal solution of acid prepared in the ordinary manner.

Method.—A large quantity of the sample is weighed out in a weighing bottle, dissolved in water—previously boiled to get rid of carbon dioxid—and made up to definite volume. Aliquot portions of this are taken for analysis. One portion is titrated with normal acid, using methyl orange as indicator, and the total alkalinity thus found noted. Another portion of the same size is transferred to a measuring flask, exactly enough barium chlorid is added to precipitate out the carbonate, and the volume made up to the mark with carbon-dioxid free water. The flask is corked, shaken, and set aside to allow the precipitate to settle. When the liquid become clear, one-third of it is drawn off by means of a pipette and titrated with normal hydrochloric acid, using phenolphthalein as indicator. This number of cubic centimeters of normal acid multiplied by 3 gives the number of cubic centimeters of normal acid corresponding to the original amount taken. The last figure obtained represents sodium hydroxid, and the difference between the first and the last figure represents sodium carbonate. For full details, see Sutton's "Volumetric Analysis."

CARBONATE AND HYDROXID. METHOD II.¹

Solutions required.—A fifth normal solution of potassium acid sulphate.

Method.—The lye is weighed out and dissolved to a definite volume in carbon-dioxid-free water, just as described in Method I, aliquot portions being taken for analysis. An aliquot portion is taken, diluted with carbon-dioxid-free water and a few drops of phenolphthalein added. An N-5 solution of potassium acid sulphate is added at the rate of about one drop per second, with constant stirring, until the pink color fades out and becomes colorless. The number of cubic centimeters of N-5 acid thus obtained which will be called "n" represents the sodium hydrate and one-half of the sodium carbonate present since the Na_2CO_3 is changed to NaHCO_3 . Methyl orange is added and the titration continued to the appearance of a pink color. Let this number of cubic centimeters be represented by m. Since this last titration represents the sodium bicarbonate present, or one-half the sodium carbonate, 2m represents all the sodium carbonate present and n—m, the sodium hydroxid present.

TOBACCO AND TOBACCO EXTRACTS.

NICOTIN. METHOD I.

Solutions required.—An alcoholic soda solution containing 6 grams of sodium hydroxid, 40 c. c. of water, and 60 c. c. of 90 per cent alcohol. A weak sodium hydroxid solution containing 4 grams of sodium hydroxid in 1000 c. c. of water. A standard sulphuric acid solution.

Method.—About 5 to 6 grams of the tobacco extract or 20 grams of finely powdered tobacco, which has been previously dried at 60° C. so as to allow it to be powdered, is weighed out into a small beaker. Ten cubic centimeters of the alcoholic soda solution is added, followed, in case of the tobacco extract, with enough c. p. powdered calcium carbonate to form a moist but non-lumpy mass. The whole is well mixed. This is transferred to a Soxhlet extractor and

¹ Cameron, U. S. Dept. of Agr., Division of Soils, Bul. 18.

extracted for about 5 hours with ether. The ether is evaporated off at a low temperature by being held over the steam bath and the residue is taken up with 50 c. c. of the weak soda solution mentioned under solutions needed. This is transferred by means of water to a Kjeldahl flask capable of holding about 500 c. c. and distilled in a current of steam, using a condenser through which water is flowing freely. A three-bend outflow tube is used, and a few pieces of pumice and a small piece of paraffine are added to the Kjeldahl flask to prevent bumping and frothing. The distillation is continued till all the nicotin has passed over. The amount of distillate is from 300 to 500 c. c., according to the amount of nicotin present. When the distillation is complete only about 15 c. c. of liquid should remain in the distillation flask. The distillate is titrated with standard sulphuric acid, using phenacetolin as indicator. One molecule of sulphuric acid is equal to two molecules of nicotin. For full details see Wiley's Principles and Practice of Agricultural Analysis, Vol. III, page 605

NICOTIN. METHOD II.¹

Solutions required.—A saturated solution of sodium hydroxide and a standard sulphuric acid solution.

Method.—From 1 to 5 grams of the extract are weighed into a 400 c. c. flask having a mouth 3 cm. in diameter. If the solution be so thick as not to flow easily, it is diluted with 1 c. c. of water. One cubic centimeter of a saturated solution of sodium hydrate is then added, and by gentle agitation mixed as completely as possible with the extract. This is allowed to stand at room temperature for twenty-four hours, during which time all ammonia is removed. Fifty cubic centimeters of N-10 caustic soda are added, and some water, and the whole subjected to distillation in a current of steam. The remainder of the method is the same as in Method I for nicotin, the final distillate being titrated against standard sulphuric acid, using phenacetolin as indicator.

NICOTIN. METHOD III.²

Solutions required.—Normal sulphuric acid. Fifth normal potassium hydroxid.

Method.—Five cubic centimeters of the solution, or extract, are weighed and placed in an extra heavy beaker. Enough of Lloyd's reagent for alkaloids (equal parts dry ferric hydrate and sodium bicarbonate) is then added to make a very stiff magna or paste. Twelve cubic centimeters of rectified petroleum ether are then added to the contents of the beaker and the whole rapidly agitated. The petroleum ether is then decanted into a small separating funnel and the operation repeated upon the pasty mass with 11, 10, 9, and 8 cubic centimeters of ether in turn. The ether extracts are mixed together in the separating funnel, and 5 cubic centimeters of normal sulphuric acid with 15 cubic centimeters of water added to the contents. The whole is rapidly shaken and the lower layer withdrawn. The ether is again washed with 10 cubic centimeters and 5 cubic centimeters of water and the washings, together with the acid extract, titrated with fifth normal potassium hydroxid, litmus being used as an indicator. Each cubic centimeter of alkali used in excess of that necessary to neutralize the acid is equal to .0324 gram nicotin.

FORMALIN.

FORMALDEHYDE. METHOD I.³

Solutions required.—Double normal sodium hydroxid and double normal sulphuric acid.

¹ Winton, U. S. Dept. of Agr., Div. of Chem., Bul. 56, p. 125.

² Lloyd, U. S. Dept. of Agr., Div. of Chem., Bul. 56, page 114.

³ Blank & Finkenbeiner Ber. 31; 17, 2979.

*Method.*¹—Three grams of the solution are weighed off into a tall Erlenmeyer flask containing 25 to 30 cubic centimeters of double normal sodium hydroxid. Fifty cubic centimeters of pure 2.5 to 3 per cent hydrogen peroxid are then gradually added during a space of three minutes through a funnel placed in the neck of the flask to prevent spurting. After standing two or three minutes, the funnel is washed with water and the unused sodium hydroxid titrated with double normal sulphuric acid, using litmus as indicator.

When analysing solutions contain less than 30 per cent of formaldehyde, the mixture must be allowed to stand ten minutes after adding the hydrogen peroxid to complete the reaction.

The percentage of formaldehyde is found by multiplying by 2 the number of cubic centimeters of soda solution used, when 3 grams of substance are taken.

Acetaldehyde reacts much more slowly with the reagent than formaldehyde, and it is doubtful whether the reaction is quantitative.

Paraldehyde reacts still more slowly with hydrogen peroxid, even in the presence of a trace of ferrous salt. Benzaldehyde is acted upon more quickly, particularly in presence of ferrous sulphate, and a considerable evolution of gas takes place, but a long time is needed to complete the reaction.

FORMALDEHYDE.—METHOD II.²

Solution required.—A standard ammonium hydroxid solution.

Method.—Ten grams of the formaldehyde solution are weighed into a flask and treated with an excess of standard ammonium hydrate solution.

The corked flask is shaken at intervals for several days. By this means the whole of the formaldehyde is converted into hexamethylamine.

The solution is then transferred to a weighed platinum dish, evaporated at a low heat—below 100° C.—nearly to dryness, and the drying is finished in a desiccator. Allowance is made for the solid residue left by the formaldehyde solution on direct evaporation.

From the weight of hexamethylamine the corresponding formaldehyde is calculated.

Instead of weighing, the excess of standard ammonia may be distilled off and determined by titration and the percentage of formaldehyde calculated from the ammonia held in combination.

FORMALDEHYDE.—METHOD III.

Solutions required.—A standard solution of ammonia and a standard solution of sulphuric acid.

Method.—Five grams of the formaldehyde solution are digested with an excess of standard ammonia solution in stoppered flask for twenty-four hours, and the remaining excess of ammonia is determined with decinormal sulphuric acid, using one or two drops of a 1 per cent solution of corallin or rosolic acid as an indicator.³

When free acid is present in the sample its quantity must be determined and taken into account.

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Approved:

JAMES WILSON,

Secretary of Agriculture.

WASHINGTON, D. C., March 7, 1902.

¹ Blank & Finkenbeiner Ber. 31: 17, 2979.

² Annual Report, Conn. Expt. Station, 1899, p. 143.

³ Zeitschr. für Untersuchung des Nahrungs-und Genussmittel, May, 1895, p. 357.